High-sensitivity NO2 sensor based on n-type InP epitaxial layers

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Abstract

The structure and sensing properties of a novel resistive NO_2 sensor based on n-type InP epitaxial layers have been presented. The studies of sensor resistance changes due to adsorbed gas NO_2 under exposures in the range from 20 to 100 ppb at a temperature of 80°C were performed. The thickness of the active InP layer changed from 0.2 to 0.4 μm. The response time and signal stability was also investigated. Furthermore, the influence of surface states and near-surface region on sensor parameters in terms of the resistance relative changes was shown from numerical simulations. The analysis of the measured photoelectron spectroscopy (XPS) spectra confirmed the complex chemical composition of the InP oxides, which give rise to the high density of surface states.

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1. Introduction

Layer-semiconductor structures are widely used for detection and monitoring of air pollution level by toxic gases. Standard commercial semiconductor gas sensors are mainly based on thick layers of metal oxides (e.g. SnO_2, ZnO) [1]. Recently, in the group of Pauly at LASMEA, B. Pascal University, Clermont-Ferrand (France), the extended research were performed on the construction and optimisation of a novel resistive gas sensor based on InP epitaxial layers, for outdoor O_3 and NO_2 monitoring in urban ambient air, working in the ppb range [2 - 4].

The epitaxial growth of III-V semiconductors allows to fabricate high quality monocrystalline n-type InP layers with well defined features as thickness, doping level, conductivity, and carrier mobility. The gas sensors with such active layers exhibited the low threshold - under 50 ppb - and short response time under NO_2 and O_3 exposure. Moreover, the InP layer initial resistance in pure air stayed very stable in time [2 - 4]. Despite these advantages, further optimisation and control of sensor parameters are needed. Thus, the systematic studies on electronic and chemical properties of thin epitaxial InP layers are necessary, in particular focused on a surface and near-surface region.

In this paper, the structure and sensing properties of a toxic gas sensor based on n-type InP epitaxial layer as well as the fabrication process of ohmic contacts have been presented. The fabricated sensors were submitted to the cycle of NO_2 exposures in the range from 20 to 100 ppb at a temperature of 80°C. The studies of sensor resistance changes due to adsorbed gas for devices with different thickness of the active InP layer (in the range from 0.2 to 0.4 μm) were performed. The response time and signal stability were also investigated. Furthermore, the influence of surface states and near-surface region on sensor parameters in terms of the resistance changes upon ion adsorption was shown from numerical simulations. In the calculations, the continuum of the U-shaped surface states in the energy gap at the free InP surface was assumed. It should be noted that the simplified standard models of semiconductor gas sensors usually neglect the role of initial surface band bending due to surface states [4]. Whereas, as it results from Ref. [5] and our previous reports [6 - 7], the surface states at InP surfaces can dramatically modify the electronic properties of near-surface region.

The analysis of the measured photoelectron spectroscopy (XPS) spectra confirmed the development of a complex InP related oxide layer at the surface, which gives rise to the high density of surface states.

2. Experimental

The structure of a resistive gas sensor based on epitaxial InP layers is shown in Fig.1. On semi-insulating iron compensated (100) InP substrates, epitaxial layers with n-type doping (N_d = 2x10^{16} cm^{-3}) were grown by molecular beam epitaxy (MBE). The thickness of the epitaxial layers was between 0.2 and 0.4 μm. The samples were rectangular with the surface area of 3.5 x 4.0 mm^2.

The ohmic contacts were made by thermal evaporation of Au (100 Å)/ Ge (350 Å) / Au (1500 Å) and under reducing atmosphere thermal annealing sequences 200°C (for 3 minutes), 250°C (for 1 minute) and 300°C (for 10 seconds). On the structure Au/Ge/Au the wire screened by Sn and tin ball were stuck, using silver paste. Each sensor was stuck onto an alumina heating substrate fitted with a screen-printed Pt resistor on its back side, allowing heating and temperature control. The operating temperature was 80°C as a result of compromise between response time of the device and induction of irreversible resistance drift of the sensor [4].

For gas tests, the sensor devices were inserted in a measuring cell and submitted to the cycles of oxidizing gas (NO_2) diluted in dry pure air exchanged with dry pure air. Gaseous flow through the measuring cell was kept constant at 50 l/h and monitored by mass flow controller. The resistance variations were recorded with a Keithley digital multimeter. The sensor resistance measurements were performed in darkness to avoid photoconductivity effect.

The photoelectron spectroscopy (XPS) measurements of the chemical properties of sensing InP surfaces were carried out using a spectrometer equipped with a Mg Kα X-ray source (1253.6 eV) and a hemispherical analyser at a constant pass energy (20 eV for high-resolution narrow scans and 50 eV for low-resolution wide scans).

3. Results and discussion

The sensor response towards oxidising gas (NO_2) at 80^0C, in terms of the relative changes of n-InP epitaxial layer resistance $\Delta R/R_0$ (layer thickness of 0.3 μm), is shown in Fig.2. The large increase of the sensor resistance upon very low NO_2 concentrations in the range from 20 to 100 ppb is evident. It results from the development of a depletion layer near the InP surface due to capturing electrons from the semiconductor bulk by adsorbed gas molecules. Moreover, the studied sensors exhibited the short response time (about 15

minutes), and good stability of their initial resistance (R_0). From our experiments we found that the initial action of NO_2 molecule at the InP surface is irreversible and can be explained in terms of surface decomposition of InP-related oxides. After many gas exposures, the action of NO_2 becomes evidently reversible (Fig.2). However, additional extended studies of the chemistry and dynamics of NO_2 interaction with InP substrate is needed for better understanding and control of the sensing process.

From Fig. 3 it is clear that the sensor relative sensitivity $\Delta R/R_0$ to NO_2 was strongly determined by the thickness of the active InP epitaxial layer, in the range from 0.2 to 0.4 μm, where the role of depletion region in conductivity is marked. The layer 0.2 μm thick exhibited the largest sensitivity however this device was also most unstable due to a strong influence of the surface on charge transport. The thickness of the layer in this case is comparable with the depletion region width.

In order to clarify the role of the surface region in sensing mechanism, the additional studies of the chemical and electronic properties of n-InP surfaces were performed as follows: (i) measurements of the XPS spectra taken before and after NO_2 submission, and (ii) theoretical calculations of the changes of relative resistance of the epitaxial InP layers before and after negative ion adsorption at room temperature.

The XPS measurements proved the presence of oxygen and carbon contaminations at the studied InP surfaces. The chosen parts of XPS spectra are summarized in Fig. 4. The analysis of P2p peak reveals the growth of InP-related oxides at the sensor surface after a several-hour cycle of oxidising gas action. It is well known fact that the native oxides at InP surfaces are extremely complex and contain simple oxides In_2O_3, P_2O_5, hydroxide $In(OH)_3$, phosphates $InPO_4$, phosphides $In(PO_3)_3$ and acid H_3PO_4 [9, 10]. On the other hand, from the critical review by Hollinger et al. [10] it results that the InP native oxide is not a mixture of stochiometric chemical compounds but rather amorphous, glass-like phase. Thus the technological control of such surfaces is difficult and further systematic studies of chemistry of InP sensor surfaces after various gas action conditions are necessary.

From these considerations it is obvious that such a free InP surface under air atmosphere conditions is a strongly disordered system. Thus, for theoretical analysis of its electronic properties we have chosen the Disorder Induced Gap State (DIGS) model of surface states by Hasegawa and Ohno [11]. These states trap the majority carriers from the semiconductor bulk, induce the depletion layer near the surface and cause the undesired pinning of the Fermi level at the surface. The U-shaped DIGS spectrum in the energy gap

$N_{SS}(E)$ consists of bonding donor-like states distributed below the so-called charge neutrality level, E_{HO}, and anti-bonding acceptor-like ones distributed above E_{HO}. An acceptor-like state is neutral if it is empty, and negatively charged by electrons taken from the conduction band, if occupied (below the Fermi level). A donor-like state is positively charged if empty, and neutral if occupied. The E_{HO} energy is a characteristic value for a given semiconductor because this quantity corresponds to the average hybrid orbital energy for sp^3 hybrid bonding. Therefore, the position of the E_{HO} level in the energy band gap does not depend on surface treatments and type of adsorbed molecules. For InP, the E_{HO} level lies 0.37 eV below the bottom of the conduction band (E_C) [11]. The corresponding $N_{SS}(E)$ function assumed in our analysis is shown in the inset in Fig. 5. The calculations of the resistance of n-InP layers were done using a computer simulator for rigorous modelling of equilibrium and non-equilibrium phenomena at semiconductor surfaces and interfaces. This program solves self-consistently the Poisson and transport equations and gives the potential V(x) and carrier concentration n(x) and p(x) dependences versus the distance from the surface. Then, using the charge concentration profiles, the total resistance of the InP layers was calculated.

The results of calculations of the n-InP relative resistance $\Delta R/R_0$ changes upon adsorption of negative ions represented by the surface fixed charge Q_{FC}, at room temperature, are summarised in Fig. 5. It is clear that the existence of surface states with a typical minimum density of 10^{12} $eV^{-1}m^{-2}$ reduces strongly the layer sensitivity to ion adsorption. Furthermore, the decrease of $\Delta R/R_0$ versus layer thickness increase is consistent with the experimental findings.

From the presented discussion it results that the InP epitaxial layer based structures are very promissing for NO_2 detection in ultra-low gas concetration range. However, their practical outdoor use in urban atmosphere requires solving further important problems, including (i) selectivity towards NO_2 in multi-gas environment and (ii) interference of water vapour, hydrocarbons and other air components on the sensor response. Our previous laboratory examinations of the action of various gases (NO_2, O_3, CO) on n-type InP-based resistive sensors, carried out in the ppm range [2], proved that the first two oxidising species had strongest influence on the sensor output resistance. However, additional systematic studies in the ppb range are necessary to clarify the problem of sensor selectivity.

The advantages of fabricated InP-based resistive sensors, such as good response times, good reproducibility of the results as well as long lifetimes, were already confirmed in the outdoor experiments performed in the air monitoring station located in the city centre of

Clermont-Ferrand (France), which is a property of AtMO AUVERGNE, the local air quality evaluation network [2, 3].

4. Conclusions

The experimental studies showed high sensitivity of the low doped n-InP epitaxial layer based gas sensor to NO_2 with extremely low concentration down to 20 ppb. The obtained response time, less then 15 minutes at 80°C, makes these sensor promising for outdoor applications.

The strong dependence of the active layer thickness was found from both experimental studies and theoretical analysis. The role of surface states and depletion layer in conduction and sensing mechanism was confirmed from computer analysis.

The creation of oxide layers upon several hours of gas submission was shown from the XPS experiment. Further systematic studies of the InP surface electronic status and its chemistry are necessary for better understanding the sensing behaviour of InP based sensor devices.

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References

[1] BARSAN N., WEIMAR U., J. Electroceramics 7 (2001), 143.

[2] TALAZAC L., BRUNET J., BATTUT V., BLANC J.P., PAULY A., GERMAIN J.P., PELLIER S., SOULIER C., Sensors and Actuators B 76 (2001), 258.

[3] BRUNET J., TALAZAC L., BATTUT V., PAULY A., BLANC J.P., GERMAIN J.P., PELLIER S., SOULIER C., Thin Solid Films 391 (2001), 308.

[4] TALAZAC L., BLANC J.P., GERMAIN J.P., PAULY A., Sensors and Actuators B 59 (1999), 89.

[5] HASEGAWA H., Solid-State Electronics 33 Supplement (1990), 201.

[6] ADAMOWICZ B., MICZEK M., WIERZBOWSKA K.B., HASEGAWA H., Rigorous analysis of the contribution of surface states to the conductivity of semiconductor thin layers, Communication at Fall Meeting of the European Materials Research Society, Warsaw, Poland 2004.

[7] WIERZBOWSKA K.B., Study of semiconductor surfaces for gas sensor application, M.Sc. Thesis, Silesian University of Technology, Gliwice, Poland (2004).

[8] ADAMOWICZ B., MICZEK M., BRUN C., GRUZZA B., HASEGAWA H., Thin Solid Films 43 (2003), 101.

[9] PAKES A., SKELDON P., THOMPSON G.E., HUSSEY R.J., MOJSA S., SPROULE G. I., LANDHEER D., GRAHAM M. J., Surface and Interface Analysis 34 (2002), 481.

[10] HOLLINGER G., BERGIGNAT E., JOSEPH J., ROBACH Y., J. Vac. Sci. Technol. A 3 (1985) 2082.

[11] HASEGAWA H., OHNO H., J. Vac. Sci. Technol. B 4 (1986), 1130.

Figure captions

Fig. 1. Scheme of the InP epitaxial layer gas sensor device.

Fig. 2. Changes of sensor resistance vs. time, submitted to different concentration of NO_2 at 80°C; InP epitaxial layer thickness d=0.3 μm.

Fig.3. Relative changes of sensor resistance ($\Delta R/R_0$) vs. time, for different thickness of n-InP epitaxial layer, exposed to 100 ppb of NO_2 at 80°C.

Fig. 4. XPS spectra from n-InP surface: a) before gas exposition, b) after cycle of NO_2 in pure air exposition.

Fig. 5. Calculated dependences of the relative changes of InP layer resistance ($\Delta R/R_0$) as a function of layer thickness (d) upon negative ion adsorption, in terms of the surface fixed charge density Q_{FC}/q, at room temperature. The solid line corresponds to the minimum density of surface states $N_{SS0} = 10^{12}$ $eV^{-1}m^{-2,}$, the dashed line represents flat band initial conditions.